

CLAIMS

1. A process to produce fluorescent substance-containing latex polymer particles, characterized in that polymerization reaction is conducted in an aqueous medium while the aqueous medium is stirred, said aqueous medium comprises:
 - (i) one or more kinds of latex-forming monomers,
 - (ii) a macromer which has, on one terminal, a polymerizable ethylenic group and has, on the other terminal, a hydrophilic polymer segment which is linked or not linked by a hydrophobic polymer segment,
 - (iii) a radical polymerization initiator, and
 - (iv) an inorganic fluorescent substance or an inorganic contrast medium.
2. A process of claim 1 wherein hydrophilic polymer segment is originated from water-soluble polymer which is selected from the group consisting of poly(ethyleneglycol), poly(vinylalcohol), poly(vinylpyrrolidone), poly(dextran), poly(dextrin) and gelatin, and wherein hydrophobic polymer segment is originated from scarcely water-soluble polymer selected from the group consisting of poly(lactide), poly(ϵ -caprolactone), poly(α - and/or β -benzyl aspartic acid) and poly(γ -benzyl glutamic acid).
3. A process of claim 1 wherein macromer has no hydrophobic polymer segment, and wherein hydrophilic polymer segment is originated from poly(ethyleneglycol).
4. A process of claim 1 wherein macromer is of two or more kinds each of which has no hydrophobic polymer segment, and each of which has, at the other terminal, a poly(ethyleneglycol) segment which carries a group selected from the group consisting of hydroxyl group, carboxyl group, aldehyde group, amino group, imino group, mercapto group, active ester-type protected hydroxyl group, active ester-type protected carboxyl group, acetal-type protected aldehyde

group, organic sulfonyl-protected hydroxyl group, reactivity-protected amino group and C₁-C₄ alkoxyl group.

5. A process of claim 1 wherein there are two macromers, the first macromer having no hydrophobic polymer segment, and having, at the other terminal, a poly(ethyleneglycol) segment which carries a group selected from the group consisting of hydroxyl group and C₁-C₄ alkoxyl group, the second macromer having no hydrophobic polymer segment, and having, at the other terminal, a poly(ethyleneglycol) segment which carries a group selected from the group consisting of carboxyl group, aldehyde group, amino group, imino group, mercapto group, active ester-type protected hydroxyl group, active ester-type protected carboxyl group, acetal-type protected aldehyde group, reactivity-protected amino group and organic sulfonyl-protected hydroxyl group, said segment of the first macromer having a chain length which is the same as, or shorter than, the chain length of said segment of the second macromer, and the molar proportion of the first macromer to the second macromer ranging from 1:5000 to 5000:1.

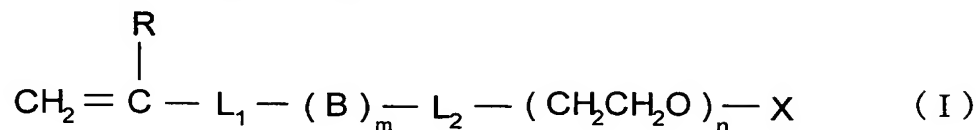
6. A process of claim 5 wherein the number of recurring unit of ethyleneglycol in the first macromer is an integer of 5 to 1200, the number of recurring unit of ethyleneglycol in the second macromer is an integer of 5 to 1200, and wherein the number of the first macromer recurring unit is the same as, or smaller than, the number of the second macromer recurring unit.

7. A process of anyone of claims 1 to 5 wherein one or more kinds of latex-forming monomers are selected from the group consisting of styrene, α -methylstyrene, *p*-bromostyrene, vinyltoluene, 1-vinylnaphthalene, C₁-C₄ alkyl (meth)acrylate and divinyl benzene.

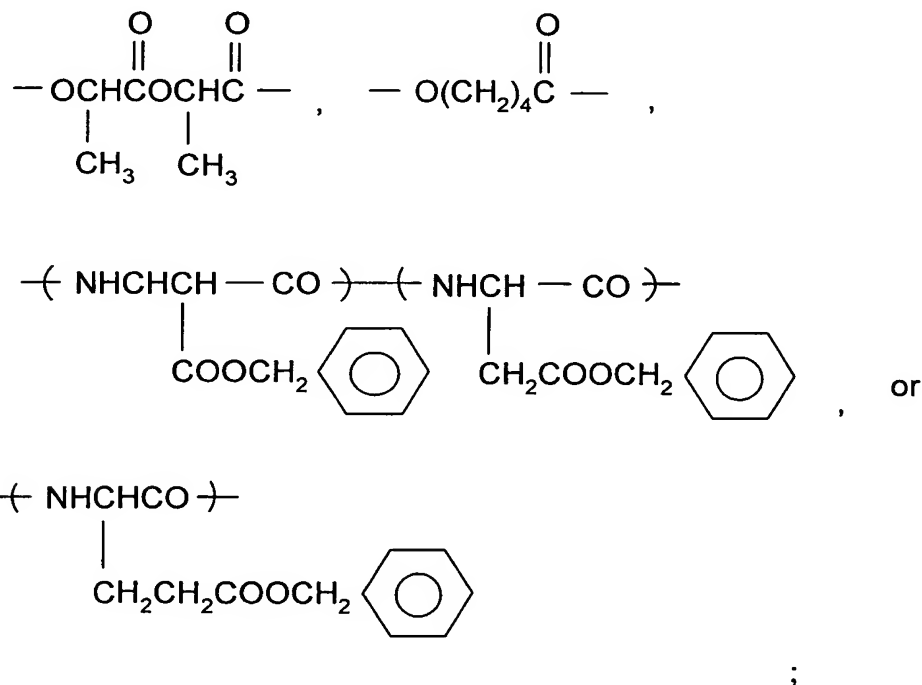
8. A process of claim 1 wherein inorganic fluorescent substance and inorganic contrast medium are in the form of chelate compound.

①

9. A process of anyone of claims 1 to 8 wherein macromer has general formula (I) as follows:



wherein R denotes hydrogen atom or C₁-C₄ alkyl group; L₁ denotes a linking group comprising a portion other than vinyl group of radically polymerizable monomer; B denotes a moiety of a structure selected from the following:



L₂ denotes a linking group comprising oxygen atom, C₁-C₄ alkylene, carbonyl, imino, or a combination of at least two thereof;

X denotes hydrogen atom, C₁-C₄ alkyl, C₁-C₄ alkylencarboxyl, C₁-C₄ alkylencarboxyl ester (said ester is exemplified by acid halide, C₁-C₄ alkyl ester and other active ester), C₁-C₄ alkyleneamino, C₁-C₄ alkylenemercapto, C₁-C₄ alkyleneacetal, C₁-C₄ alkyleneoxycarbonylimidazol; m denotes an integer of 0 to 500, and n denotes an integer of 5 to 1200.

10. Hydrophobic core-hydrophilic shell type latex polymer particles

which include, in their hydrophobic core domain, inorganic fluorescent substance or inorganic contrast medium, said latex polymer particles having an average particle size of 0.001 to 5 μm , and being formed by radical polymerization in an aqueous medium which comprises:

- (a) 0.5 to 99.5 % by weight of one or more kinds of latex-forming monomer,
- (b) 0.5 to 99.5 % by weight of macromer which has, on one terminal, a polymerizable ethylenic group and has, on the other terminal, a hydrophilic polymer segment which is not linked by a hydrophobic polymer segment [this macromer includes two kinds of macromers each of which has, on said the other terminal, a poly(ethyleneglycol) segment which carries a group selected from the group consisting of hydroxyl group, carboxyl group, aldehyde group, amino group, imino group, mercapto group, active ester-type protected hydroxyl group, active ester-type protected carboxyl group, acetal-type protected aldehyde group, organic sulfonyl-protected hydroxyl group, reactivity-protected amino group and $\text{C}_1\text{--C}_4$ alkoxyl group, recurring unit of said ethyleneglycol being 5 to 1200].

11. Hydrophobic core-hydrophilic shell type latex polymer particles of claim 10 wherein there exist two macromers, the first macromer having no hydrophobic polymer segment, and having, at the other terminal, a poly(ethyleneglycol) segment which carries a group selected from the group consisting of hydroxyl group and $\text{C}_1\text{--C}_4$ alkoxyl group; the second macromer having no hydrophobic polymer segment, and having, at the other terminal, a poly(ethyleneglycol) segment which carries a group selected from the group consisting of carboxyl group, aldehyde group, amino group, imino group, mercapto group, active ester-type protected hydroxyl group, active ester-type protected carboxyl group, acetal-type protected aldehyde group, reactivity-protected amino group and organic sulfonyl-protected hydroxyl group; said segment of the first macromer having a chain length which is the same as, or shorter than, the chain length of said segment of the second macromer; and

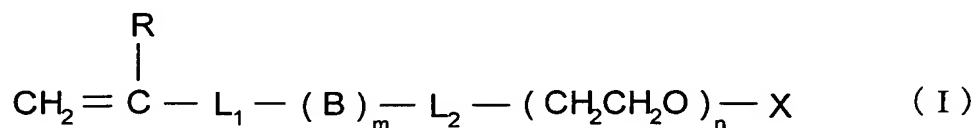
the molar proportion of the first macromer to the second macromer ranging from 1:5000 to 5000:1.

12. Hydrophobic core-hydrophilic shell type latex polymer particles of claim 10 wherein the number of recurring unit of ethyleneglycol in the first macromer is an integer of 5 to 1200, the number of recurring unit of ethyleneglycol in the second macromer is an integer of 5 to 1200, and wherein the number of the recurring unit of the first macromer is the same as, or smaller than, the number of the recurring unit of the second macromer.

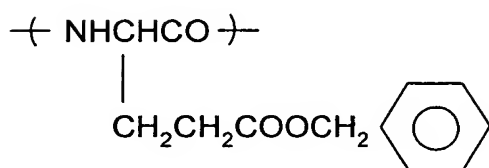
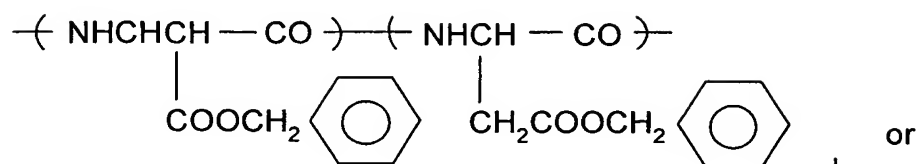
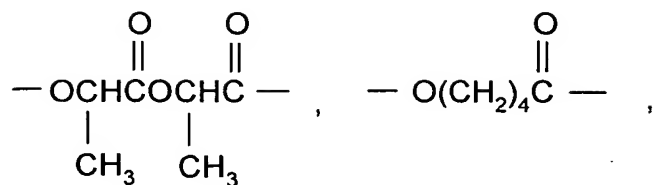
13. Hydrophobic core-hydrophilic shell type latex polymer particles of anyone of claims 10 to 12 wherein one or more kinds of latex-forming monomers are selected from the group consisting of styrene, α -methylstyrene, *p*-bromostyrene, vinyltoluene, 1-vinylnaphthalene, C₁-C₄ alkyl (meth)acrylate and divinyl benzene.

① 14. Hydrophobic core-hydrophilic shell latex polymer particles of anyone of claims 10 to 13 wherein inorganic fluorescent substance and inorganic contrast medium are a rare-earth metal which belongs to lanthanoid in periodic table of the element or a chelate compound thereof.

① 15. Hydrophobic core-hydrophilic shell type latex polymer particles of anyone of claims 10 to 14 wherein macromer has general formula (I) as follows:



wherein R denotes hydrogen atom or C₁-C₄ alkyl group; L₁ denotes a linking group comprising a portion other than vinyl group of radically polymerizable monomer; B denotes a moiety of a structure selected from the following:



;

L_2 denotes a linking group comprising oxygen atom, C_1 - C_4 alkylene, carbonyl, imino, or a combination of at least two thereof;
 X denotes hydrogen atom, C_1 - C_4 alkyl, C_1 - C_4 alkylencarboxyl, C_1 - C_4 alkylencarboxyl ester (said ester is exemplified by acid halide, C_1 - C_4 alkyl ester and other active ester), C_1 - C_4 alkyleneamino, C_1 - C_4 alkyleneamercapto, C_1 - C_4 alkyleneacetal, C_1 - C_4 alkyleneoxycarbonylimidazol; m denotes an integer of 0 to 500, and n denotes an integer of 5 to 1200.